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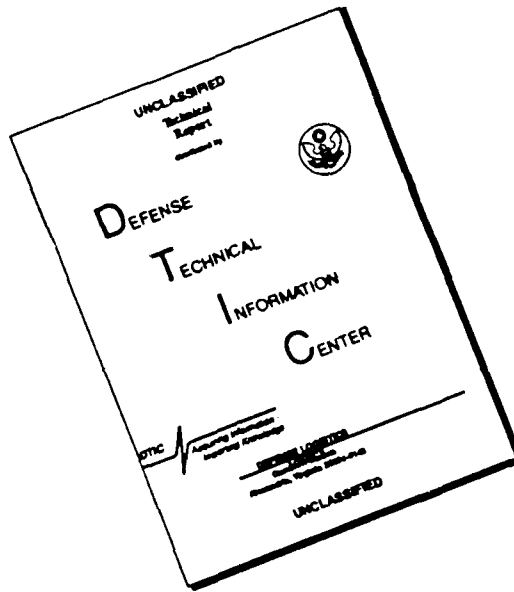
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PROGRESS REPORT

We present below a brief description of some of the results that have been obtained during this past year on the program on the electronic structure of complex systems and the origin of their electronically driven phase transitions. The high level of scientific progress made during this past year on the proposed research will become apparent from the accomplishments reported briefly here and from the list of publications which have resulted from AFOSR support.

A. High Field Superconductivity of Chevrel Phase Compounds

As indicated in last year's proposal, the properties of the Chevrel phase compounds, particularly $SnMo_6S_8$ and $EuMo_6S_8$, are of great scientific and technological interest because of their unusual high magnetic field properties including the enhancement of the upper critical field H_{c2} observed when Eu is added to $SnMo_6S_8$. For example, up to an Eu concentration of 0.5, T_c is hardly changed with the depression occurring abruptly only at high concentration. This behavior is contrary to observations on all other materials with the addition of a local magnetic moment and the theory of Abrikosov and Gor'kov.

The large increase in H_{c2} found when Eu is doped into $SnMo_6S_8$ has attracted great interest. In order to explain this phenomenon, Fradin, et al. postulated, on the basis of their combined Mössbauer and NMR studies, that although positive at the Eu site, the induced conduction electron polarization at the Mo site would be negative. Thus, this negative spin-polarization at the site where the superconducting d electrons reside serves to screen out the applied magnetic field and to give H_{c2} values which are among the largest known (~400 k Gauss).

We have carried out an extensive theoretical study of the origin of high field superconductivity and/or magnetism in a number of Chevrel phase ternary compounds, $M\,Mo_6X_8$ (M=Sn,Eu,Gd and X=S and/or Se) based on self-consistent

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linear muffin-tin orbital (LMTO) energy band calculations using the local density approach (Hedin, et al. exchange correlation) for the paramagnetic structures and, during this last year, using local spin density formalism (Gunnarsson-Lundqvist) for the ferromagnetic structures. All electrons and all 15 atoms/cell were included with the core electrons (including the 4f's) recalculated in each iteration in a fully relativistic representation and the conduction electrons treated semirelativistically (all relativistic terms except spin-orbit).

Superconductivity was found to be due to the high Mo d-band density of states (DOS) at E_F resulting from the unusual large charge transfer of Mo electrons to the chalcogen sites. There is also a large charge transfer from the metal site to the cluster (~2 electrons in Sn and Eu) giving essentially no occupied conduction bands, for example, at the Eu site and a divalent ion isomer shift in very good agreement with the experiments of Dunlap, et al. The conduction-electron DOS at the Eu site was found to be reduced by an order of magnitude from its metallic state value — in close agreement with their spin-lattice relaxation rate measurements. This low conduction-electron DOS yields very weak coupling of the 4f electrons to the conduction electrons and only a very weak Ruderman-Kittel-Kasuya-Yosida magnetic interaction showing why all the Chevrel rare-earth compounds — except Ce and Eu — are super-conducting despite their having large local magnetic moments.

The unusually high upper critical fields, H_{c2}, in these materials was found to be due to the unusually flat energy bands near E_F. The ferromagnetic (spin-polarized) results for the Eu- and Gd-compounds show a net small but positive magnetic moment on the metal site and a small but negative induced spin magnetic moment on the Mo site in the Eu compounds. Fermi-contact contributions to the hyperfine field were calculated and found to be in good

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agreement with the Eu Mössbauer results and the negative NMR Knight shift results of Fradin, et al. These results demonstrate theoretically for the first time the validity of the Fischer, et al. and Fradin, et al. conclusion that the Jaccarino-Peter mechanism is responsible for the large increase in the H_{c2} when large concentrations of Eu magnetic impurities are added to $SnMo_6S_8$. Finally, we have calculated Stoner factors for the paramagnetic phase and spin magnetization densities for the ferromagnetic phase in order to understand qualitatively the origin of the different behavior observed for $GdMo_6S_8$ and $EuMo_6S_8$.

B. Superconductivity and Magnetism in C15 Compounds

As indicated last year, we proposed to continue an extensive study of the un-usual magnetic and superconducting properties of the C15 compounds (formula AB_2 and 6 atoms/unit cell) initiated earlier. These properties range from the itinerant ferromagnetism in $ZrZn_2$ and the proposed itinerant antiferromagnetism of $TiBe_2$ (also under study with neutrons by Felcher, Sinha, et al.) to the high temperature superconducting systems like ZrV_2 and HfV_2 which undergo phase transitions (like the high T_c superconducting A15 compounds) at moderately high temperatures and the superconducting/Kondo systems, $LaAl_2$ and $CeAl_2$.

As was emphasized last year, interest in these systems had been revitalized following the report of itinerent antiferromagnetism in $TiBe_2$ by Matthias, et al. This discovery followed the expectation raised by the theoretical proposal of Enz and Matthias that the itinerent ferromagnetism of $ZrZn_2$ arises from inhibited 'p-state' pairing. In this view, the Cooper pair interaction is thought to become repulsive at short distances (s-state) due to a dominant soft phonon, leaving only p- and higher states to be attractive. Thus the s-state repulsion would contribute sufficiently to the Stoner factor to tip the balance toward magnetism and to prevent the occurrence of p-state superconductivity. They further predict that above a critical pressure at which the magnetism is destroyed in $ZrZn_2$, p-state pairing superconductivity would appear and in $TiBe_2$ coexist with any antiferromagnetic ordering.

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As in the case of the Chevrel compounds, we have studied several of these complex C15 compounds by means of all-atom, all-electron self-consistent LMTO energy band calculations. For these compounds the valence states were treated in a semi-relativistic scheme, where the mass-velocity and Darwin terms are included in the solution of the Dirac equation, but with the smaller spin-orbit terms excluded. Total and partial (by atom type and l-values) DOS, electron-phonon coupling parameter, λ, and T_c values and their behavior under pressure were determined.

Extensive results have now been obtained for $TiBe_2$ and $ZrZn_2$ in their paramagnetic states. In addition, for better understanding magnetism/super-conductivity in these C15 compounds, the high T_c superconductor ZrV_2 and the ultra-low T_c superconductor YAl_2 were also considered. The results obtained [total and partial (by atom type and l-value) DOS, important Fermi-surface nesting, Stoner-like parameters to describe the conditions for magnetism, electron-phonon coupling parameter, λ, and T_c values and their behavior under pressure] have been used to provide a qualitative understanding of magnetism/superconductivity and to predict the possibility of superconductivity in $ZrZn_2$ and $TiBe_2$ with application of pressure without invoking p-state pairing.

More recently we have carried out self-consistent, spin-polarized LMTO calculations on the (stoichiometric) compounds $ZrZn_2$ and $TiBe_2$, and have compared the resulting ferromagnetic spin distributions with the neutron measurements on $ZrZn_{1.9}$ and $TiBe_{1.8}Cu_{0.2}$. The initial configuration assumes a small moment ($\sim 0.03\mu_B$/atom) in each compound, which in the subsequent iterations grow to the converged results.($0.19\mu_B$ for $TiBe_2$ and $0.12\mu_B$ for $ZrZn_2$). Paramagnetic band results show a high Zr/Ti d-DOS which makes a magnetic Stoner splitting of the bands energetically favorable. The spin-polarized results also show that the moment is concentrated on these sites, and the higher Ti than Zr moment is reflected in the higher Ti DOS.

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The radial spin distributions show the rather itinerant character of the magnetic moments, more so for $ZrZn_2$ than $TiBe_2$, which is in agreement with the measured spin density maps. However, the deduced spin form factors, including the small contribution from the Be and Zn sites, give somewhat less contracted form factors than from the experiments, i.e. less itinerant spin-density.

In summary, we find ferromagnetic states in both compounds, with the moments due to the Zr and Ti d-electrons and the spin distributions, are in good agreement with neutron data on non-stoichiometric samples.

C. Electronic Structure of $TaSe_3$, A Linear Trichalcogenide Compound

Last year, we proposed to study $TaSe_3$, a "linear" chain transition metal trichalcogenide which has been found to exhibit unusual properties. The trichalcogenide compounds have structures made up of infinite chains of trigonal prisms TX_6 extending parallel to the b axis of their monoclinic cells. For example, the crystal structure of $TaSe_3$ is quite complex having four formula groups per unit cell for a total of 16 atoms per unit cell of the monoclinic structure. Unlike the trichalcogenides of the group IV transition elements as well as the sulfide compounds of the group VB which are semiconductors, $TaSe_3$ shows metallic behavior from room temperature down to the helium range. It is a superconductor at 2 K and shows large effects with applied pressure. The application of pressure causes its critical temperature to <u>increase</u>, unlike the case of $NbSe_3$.

We have initiated self-consistent LMTO energy band calculations including all electrons and all atoms in the unit cell within the local density functional formalism for exchange and correlation. Energy band structure, density of states, Fermi surface and charge densities are being determined for comparison with experiment. In the calculations, some of the Se atoms in the $TaSe_3$ structure have been assigned an averaged potential so that in the calculations there are 6 inequivalent atom types. The basis includes s-p and d for all atoms leading

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to a secular equation of the dimension 144x144. The self-consistent convergence is to a shift of 3 mRy, or smaller, in any occupied eigenvalue. For the final calculations, 54 k-points were used.

The results to date show charge transfer from the Se to the Ta atoms. This leads to a "dip" in the Ta-d band DOS at the position of the Fermi energy. (E_F). An inspection of the bands around E_F indicates that this is due to some overlapping in part of the Brillouin zone.

D. Metamagnetic Phase Transition in Pd Metal

Itinerant metamagnetism in high magnetic fields has been a subject of continuing interest since its prediction for Pd and other strongly exchange-enhanced metals. For such a field induced first-order phase transition from the paramagnetic to the ferromagnetic state, free energy arguments focused on metals which have a maximum in the temperature dependence of the magnetic susceptibility. While metamagnetic behavior has been inferred or observed for several systems, no first principles theoretical calculations have been reported in support of such observations. We have carried out the first ab initio theoretical study of the electronic band structure, magnetic susceptibility and magnetization in the presence of external magnetic fields which demonstrates the onset of a metamagnetic transition. At low fields our results for Pd metal agree very well with the measured (exchange enhanced) susceptibility and the qualitative behavior of the g-factors determined recently by de Haas-van Alphen experiments. At a high critical field, B_{crit}, there is a large step-like increase in the magnetization, m. These results indicate that while B_{crit} is too large (~300 T) to permit the observation of metamagnetism in pure Pd, its observation at lower critical fields is likely for Pd doped with low concentrations of magnetic impurities such as Ni or in the Au/Pd/Au

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sandwiches which have been found recently by Brodsky and Freeman to have enormously enhanced X values at low temperatures. They also lend support to recent interpretations of the positive deviations at high B from the linear dependence of the magnetization at low B as indicating possible metamagnetic behavior in $TiBe_2$.

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